



Oceanic molybdenum isotope fractionation: Diagenesis and hydrothermal ridge-flank alteration

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[1] Isotopic analyses of dissolved molybdenum are presented for sediment pore waters from a reducing sedimentary basin and for fluids from a low-temperature ridge flank hydrothermal system. $\delta^{98/95}\text{Mo}$ in these fluids range from 0.8 to 3.5‰ (relative to a laboratory standard), demonstrating that marine sedimentary reactions significantly fractionate Mo isotopes. Within the upper 3 cm of sediment, manganese oxide dissolution produces an isotopically light fluid relative to seawater (mean of four analyses = $2.1 \pm 0.1\text{‰}$ versus seawater = $2.3 \pm 0.1\text{‰}$). Below 6 cm depth, authigenic Mo uptake results in an isotopically heavier fluid (up to 3.5‰) indicating that reducing sediments are likely to be a net sink for isotopically light dissolved Mo. In contrast, fluid circulation within a low-temperature ridge-flank hydrothermal system is a source of isotopically light Mo to the ocean having an end-member fluid of $\sim 0.8\text{‰}$.

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1. Background

1.1. Mo Geochemistry

[2] Mo has seven stable isotopes, ranging from mass 92 to 100, and multiple oxidation states. Mo is present in seawater as the stable oxyanion, MoO_4^{2-} . It has a residence time of ~ 800 ky [Emerson and Husted, 1996; Colodner et al., 1995], is nearly conservative in the oceanic environment, and has a relatively high salinity normalized dissolved concentration of ~ 100 nM [Morris, 1975; Collier, 1985]. Mo exhibits small systematic water column variations [Collier, 1985] and is an element of known biological importance (e.g., Howarth and Cole [1985], Howarth et al. [1988], Marino et al. [1990], Paulsen et al. [1991], Cole et al. [1993], and others).

[3] Extensive work to date has demonstrated that Mo is sequestered in anoxic marine sedimentary environments (e.g., Bertine and Turekian [1973], Brumsack and Gieskes [1983], Brumsack [1986], Emerson and Husted [1996], Calvert and Pedersen [1993], Colodner et al. [1995], Piper and Isaacs [1995], Crusius et al. [1996], Dean et al. [1997], Morford and Emerson [1999], and others). The exact details of sedimentary Mo uptake during diagenesis and the particular Mo-containing solid phases involved in these systems remain unclear [e.g., Helz et al., 1996; Erickson and Helz, 2000]. However, the general sequence of Mo behavior in marine sediments is that (1) Mo is incorporated into oxic sediments in association with metal oxides, (2) Mo is then released during oxide reduction, (3) Mo is removed into anoxic sediments in the presence of HS^- [e.g., Bertine, 1972; Berrang and Grill, 1974; Shimmield and Price, 1986; Shaw et al., 1990; Emerson and Husted, 1996; Zheng et al., 2000; Erickson and Helz, 2000]. Because of its low (lithogenic) background concentration in marine sediments and its relatively high authigenic concentration in reducing marine settings, Mo has attracted significant attention as a paleochemical tool (references as above). Given its isotopic range, the potential for redox shifts in the oceanic environment, its participation in biological processes, and its relatively high concentration in ocean water, it is likely that significant isotopic

fractionation may occur as Mo is cycled through the oceans. Consequently, molybdenum isotopes are a natural choice for exploration as a geochemical tool.

1.2. Mo Isotopes

[4] Stable element isotopes have proven to be invaluable for studying biological as well as abiological processes in modern and past oceans. The stable isotopes of oxygen and carbon, for example, are among the most commonly employed paleotracers. With the advent of multiple collector plasma source mass spectrometry (MC-ICPMS) detailed research on transition metal isotopes has become possible [Halliday et al., 1995], and it has been demonstrated that transition elements undergo measurable isotopic fractionation (e.g., reviews in Halliday et al. [1998] and Anbar [2001]).

[5] There are few published Mo isotope data from MC-ICPMS [Anbar et al., 2001; Barling et al., 2001; Siebert et al., 2001, 2002]. Contemporary manganese crusts, clastic sediments, and pelagic clays all exhibit values that are lighter ($\delta^{98/95}\text{Mo} = -0.8$ to 0.9‰) than parent seawater (2.3‰) [Anbar et al., 2001; Barling et al., 2001; C. Siebert et al., Oceanic molybdenum isotope fractionation: Sources, sinks and the secular evolution over 60 Ma manuscript submitted to *Earth and Planetary Scientific Letters*, 2002, hereinafter referred to as Siebert et al., submitted manuscript, 2002]. From each of these studies it appears that fractionation of Mo isotopes occurs during removal from solution, consistent with laboratory studies [Barling and Anbar, 2001]. Furthermore, although there is an isotopic offset, steep Mo concentration gradients within Fe-Mn crusts are evidence that Mo is not homogenized after deposition [Siebert et al., submitted manuscript, 2002] so that Fe-Mn crusts are a potentially viable recorder of seawater Mo isotopes and thus a possible indicator for paleo-oxidation state of the oceans [Barling et al., 2001; Siebert et al., submitted manuscript, 2002].

1.3. Study Sites

[6] Pore water Mo and Mo isotopic data are presented from the Santa Monica Basin, which



is located in the Southern California Borderlands region. This basin is characterized as having low bottom water dissolved oxygen concentrations ($<5 \mu\text{M}$) and organic carbon oxidation rates of $\sim 2 \text{ mmol m}^{-2} \text{ d}^{-1}$. Intense near-surface Fe and Mn cycling further characterize the sediments in this basin [Shaw *et al.*, 1990]. The significance of this basin with respect to Mo isotopic geochemistry is that sulfate reduction represents a significant diagenetic pathway for organic carbon decomposition within this basin [Berelson *et al.*, 1996], thus allowing us to identify the net effect of this process as well as Fe and Mn cycling on sedimentary Mo fractionation. Furthermore, reducing environments are a net sink for oceanic Mo.

[7] Mo isotopic ratios were also analyzed on samples from warm hydrothermal springs on Baby Bare, a basaltic outcrop overlying 3.5 Ma crust and ~ 100 km east of the Juan de Fuca Ridge [Mottl *et al.*, 1998; Wheat and Mottl, 2000; Becker *et al.*, 2000; Wheat *et al.*, 2002]. A flat turbidite plain that covers most of the seafloor with 200–600 m of sediment surrounds this site, in the middle of Cascadia Basin. Three springs were located on Baby Bare and have measured temperatures that range from 24.5°C to 25°C . Their waters are derived from a warmer ($\sim 63^\circ\text{C}$) basement formation fluid that has cooled conductively during fluid ascent [Davis *et al.*, 1997; Fisher *et al.*, 1997; Mottl *et al.*, 1998]. The general pattern for fluid circulation is one in which cold oxygenated bottom seawater flows into basaltic basement, presumably 52 km away at Grizzley Bare, warms and undergoes water-basalt reactions in basement. In concert with these reactions, diffusive fluxes to or from the overlying sediment change the fluid composition as this basement formation water advects toward Baby Bare where it vents as warm altered seawater [Wheat *et al.*, 2000; Hutnak *et al.*, 2001; Wheat *et al.*, 2002]. The significance of this form of hydrothermal system is that similar systems on ridge flanks remove most of the crustal convective heat loss [Sclater *et al.*, 1980; Stein and Stein, 1994]. Because this loss is at relatively low temperatures, the required seawater flux is large. This large flux coupled with even a small chemical anomaly can

result in global fluxes that impact global biogeochemical budgets [e.g., Bloch and Bischoff, 1979; Maris *et al.*, 1984; Mortlock *et al.*, 1993; Mottl and Wheat, 1994; Elderfield and Schultz, 1996; Wheat *et al.*, 1996].

2. Methods

[8] Dissolved Mo concentrations were analyzed using a Fisons/VG model PQ2⁺ (hydrothermal samples) or Axiom high-resolution ICP-MS (pore water samples). Pore water samples were measured by isotope dilution using a ^{100}Mo isotope spike. Mo isotopes were analyzed using a Nu Instruments multicollector ICP-MS at the University of Bern [Siebert *et al.*, 2001]. Briefly, we used a Mo double spike, ^{97}Mo and ^{100}Mo , and report Mo isotopic fractionation as $\delta^{98/95}\text{Mo}$, relative to a Johnson Matthey ICP standard, lot 602332B. Seawater Mo has a $\delta^{98/95}\text{Mo} = 2.3\text{‰}$ relative to this standard [Siebert *et al.*, 2001]. Individual sample uncertainties (2σ) are typically 0.1‰ (2σ) with the external reproducibility also being 0.1‰ (2σ). The minimum quantity of Mo required was $\sim 0.02 \mu\text{g}$ Mo when using an Aridus[®] desolvating nebulizer.

[9] Sediment cores were collected using a multiple-corer. Cores were sectioned under a nitrogen atmosphere at 4°C , and samples were centrifuged at 8000 rpm for ~ 15 min at 4°C . Fluid samples were then filtered ($0.45 \mu\text{m}$) under a nitrogen atmosphere and acidified using triple-distilled HCl. Further details of sample processing are described elsewhere [e.g., McManus *et al.*, 1998]. Spring waters were sampled using the Ti-Major sampler with an in-line sampling system [Massoth *et al.*, 1989]. We present a subset of these samples from two of the three springs. The spring at marker 17 vented directly from basaltic basement, thus providing the most pristine formation fluids to the seafloor [Wheat *et al.*, 2002]. In contrast, the springs at marker 15 vented through a thin veneer of sediment (<0.7 m). Diagenetic reactions within this sediment veneer locally alter the formation fluid as it ascends. One consequence of the hydrogeology of this particular system is that spring fluids interact with young (at the site of venting) and old (imme-



diately above the sediment-basalt interface) sediment and basaltic basement.

3. Mo Isotopes in Sediment Pore Water

[10] Within the upper 6 cm of sediment, marine pore waters from the Santa Monica Basin are isotopically lighter than the overlying seawater (Figure 1a). This isotopically light Mo is coincident with a zone of intense Mn and Fe cycling that produces a subsurface Mo maximum and high concentrations of dissolved Mn and Fe in the pore fluids (Figures 1b and 1c). Likewise a Mn-rich solid-phase layer (enriched Mn/Al ratios) decreases through the upper 5–10 cm, approaching the lithogenic Mn/Al ratio at depth (Figure 1d). We hypothesize that the isotopically light pore water Mo (upper 6 cm) results from the liberation of isotopically light Mo during oxide dissolution. This hypothesis is consistent with previous results showing Mn-oxides to be isotopically lighter (by ~3‰) relative to the fluids in which they are formed [Barling *et al.*, 2001; Barling and Anbar, 2001; Siebert *et al.*, submitted manuscript, 2002].

[11] The isotopic increase below ~6 cm is coincident with a decrease in pore water Mo concentrations (Figure 1b). These data suggest that authigenic Mo formation fractionates Mo isotopes with the lighter isotopes being preferentially taken up in authigenic phases. Thus these data suggest that sedimentary Mo isotopes have potential as a proxy for sedimentary redox conditions. Furthermore, given that reducing sediments are an important sink for the global Mo balance, these data offer one possible explanation for why seawater Mo isotopes are isotopically heavier than most other natural samples [Siebert *et al.*, 2001; Barling *et al.*, 2001]; diagenetic fractionation during authigenic Mo uptake will leave behind a heavier oceanic pool.

[12] The fractionation as Mo is authigenically sequestered in anoxic sediments can be evaluated quantitatively using a reaction-diffusion Rayleigh distillation approach. We only use data below 6 cm under the assumptions that release from Mn oxides is complete by this depth and that uptake is irreversible. Thus, for each isotope

$$0 = D_i C_i'' - k_i C_i, \quad (1)$$

where, at steady state, D , C , and k are the diffusivity, concentration, and rate constants for each isotope, respectively, and the double prime indicates the second derivative. The solution for this equation is

$$C_i = C_{i,0} \exp(-az), \quad (2)$$

where $a = (k_i/D_i)^{0.5}$ and $C_{i,0}$ is the concentration of the isotope at the reference depth (here 6 cm). We assume that both isotopes have the same diffusivity and that the rate constants are defined as follows:

$$k_2 = \alpha(k_1), \quad (3)$$

where α is the separation constant between the two isotopes. The concentration ratio between the two isotopes is then

$$C_2/C_1 = (C_2/C_1)_0 \exp([a_1 - a_2]z). \quad (4)$$

After rearrangement and taking the natural log of both sides,

$$\ln(R_z/R_0) = z(1 - \alpha^{0.5})a_1. \quad (5)$$

Because a_1 can be found from

$$C_1/C_{1,0} = \exp(-a_1 z), \quad (6)$$

thus

$$R_z = R_0 F^b, \quad (7)$$

where $F = C_1/C_{1,0}$, which is the fraction of Mo remaining in pore water relative to the reference depth ($C_{1,0}$), R_z is the isotopic ratio at depth, z , and the exponent, $b = \alpha^{0.5} - 1$. By fitting the data ($\ln R_z$ versus $\ln F$) below 6 cm (chosen as the reference depth, $z = 0$), we arrive at the slope, b , and calculate α to be 1.0070 for these particular sediments (Figure 1e). Because no other data of this kind exist, we cannot compare this value to other settings; however, it is quite possible that α will vary under diagenetic conditions that are more (or less) favorable to authigenic Mo uptake.

[13] From a budgetary perspective, anoxic sediments are a potentially important sink for oceanic Mo [e.g., Morford and Emerson, 1999]. If the isotopic fraction (with respect to seawater) presented here is typical for anoxic sediments and anoxic

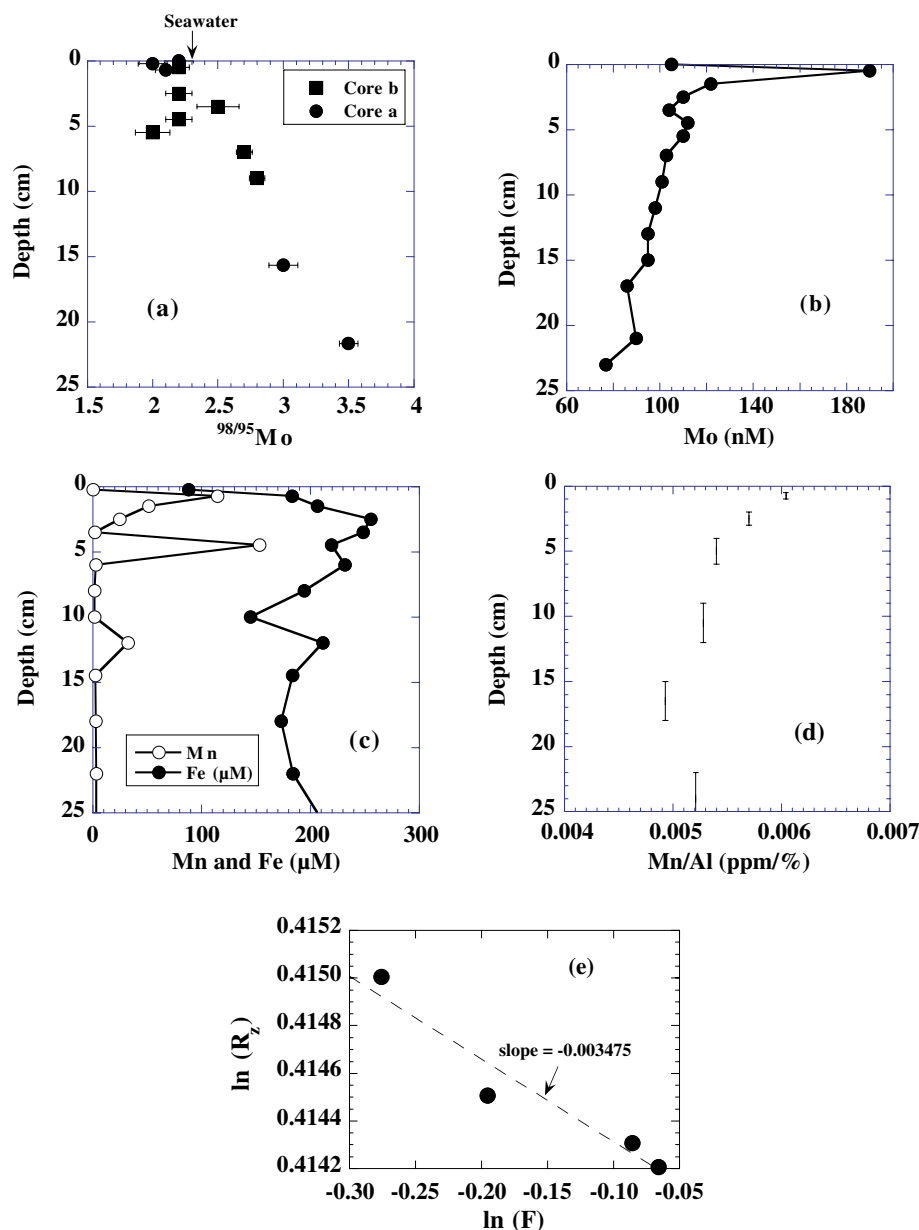


Figure 1. Pore water and solid-phase profiles from Santa Monica Basin. (a) $\delta^{98/95}\text{Mo}$ and (b) Mo concentration and as a function of depth in sediment pore waters. The high pore water Mo concentration apparent immediately below the sediment-water interface is likely caused by Mn reduction in this region [e.g., Shaw *et al.*, 1990]. Note the different $\delta^{98/95}\text{Mo}$ symbols from the Santa Monica basin represent samples taken from two separate companion cores. Both cores were collected during the same multicore deployment during July 2001. (c) Mn and Fe pore water profiles from Santa Monica Basin. These data were collected in March 1994 [McManus *et al.*, 1997, 1998]. In the case of both Fe and Mn, this cycling produces substantial benthic effluxes from the sediments [McManus *et al.*, 1997, 1998]. (d) The Mn/Al ratio as a function of depth in Santa Monica basin. These data were also presented by McManus *et al.* [1999] and are the companion solid phases to the dissolved iron and manganese data in Figure 1c. (e) The $\ln R_z$ as a function of $\ln F$. Slope defines b as described in the text.

sediments are a major Mo sink, then Mo fractionation during anoxic uptake could provide a source of isotopically heavy Mo that maintains the oceans isotopic composition. In addition, the other major

Mo sink, oxic sediments [e.g., Morford and Emerson, 1999 and references therein], also fractionates Mo leaving behind a heavier reservoir [Barling *et al.*, 2001; Siebert *et al.*, submitted manuscript,

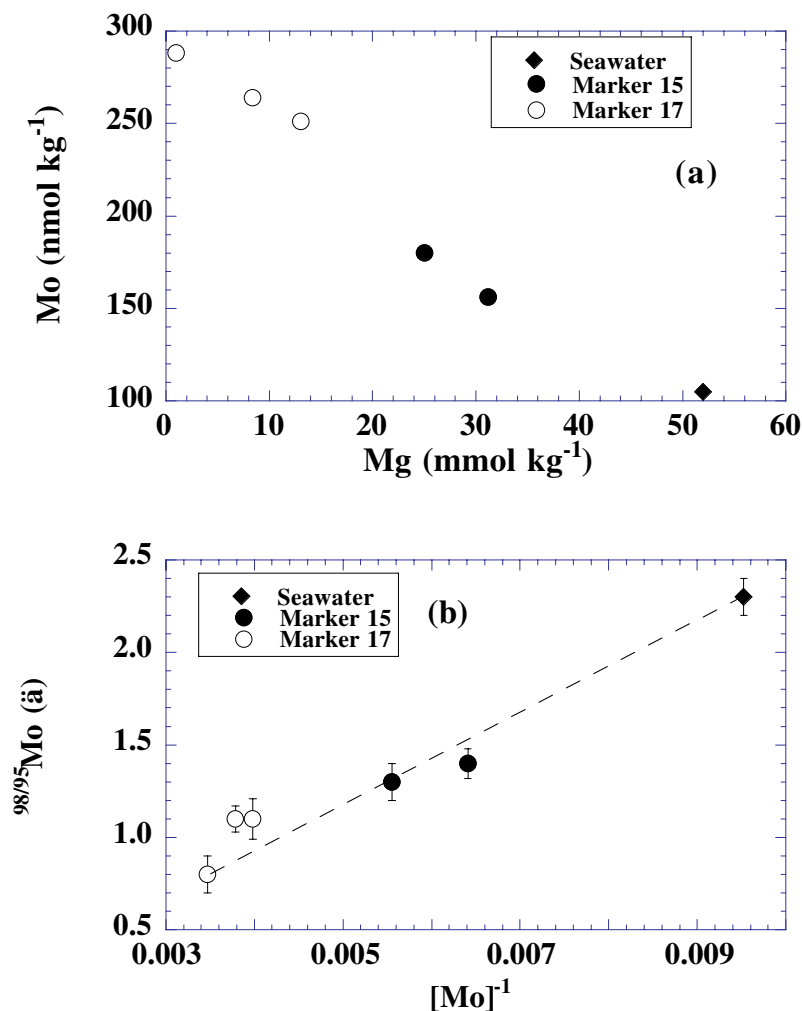


Figure 2. Mo in fluids from Baby Bare Hydrothermal Springs. (a) Dissolved Mo as a function of Mg from Baby Bare hydrothermal springs. Data were previously reported in *Wheat et al.* [2002]. (b) $\delta^{98/95}\text{Mo}$ as a function of Mo^{-1} in same samples as in Figure 2a. The dashed line is a mixing line between possible end-members.

2002]. The hypothesis that isotopic fractionation during Mo uptake within these combined sinks, although a plausible explanation for why ocean water is isotopically heavy, requires better constraints on both the oceanic Mo budget and the Mo isotope budget, neither of which is well-constrained.

4. Mo Isotopes in a Sediment-Hosted Ridge-Flank Hydrothermal System

[14] Each of the springs has Mo concentrations that are greater than bottom seawater, indicating that this system is a net source of Mo to the oceans [*Wheat et al.*, 2002]. The formation water end-member concentration is 297 nmol Mo kg⁻¹, based

on extrapolating data from the spring at marker 17 to a zero Mg concentration (Figure 2a). This result is ~3 times the concentration in bottom seawater. These fluids have a $\delta^{98/95}\text{Mo}$ that is isotopically light compared to bottom seawater, and the limited data available suggest first-order linear mixing between hydrothermal and seawater end-members that have $\delta^{98/95}\text{Mo}$ of 0.8 and 2.3‰, respectively (Figure 2b). That being said, *Wheat et al.* [2002] surmise that at least part of this excess Mo is derived from the sediment. For example, *Mottl et al.* [2000] present Mn data that confirm the existence of a sedimentary Mn flux to basement near Baby Bare. Similarly, the mobilization of Mo in the sediments overlying basaltic basement and the

diffusion of this Mo into basement formation fluids is possible in this setting. The hypothesis that Mo in these spring fluids are derived from sediment-fluid interactions at the sediment-basement interface is consistent with the proposal made here that sedimentary authigenic Mo will be isotopically light relative to its source. After deposition, the isotopically light (relative to seawater) sedimentary Mo is ultimately (millions of years later) remobilized and diffuses into basaltic basement.

[15] An alternative or additional hypothesis is that low-temperature seawater-basalt interactions generate an isotopically light, Mo-enriched fluid. With regard to this latter point, magmatic rocks are isotopically light relative to seawater [Siebert et al., submitted manuscript, 2002] and could thus be a source of isotopically light Mo. Regardless of the mechanism for fluid formation, low-temperature ridge flank springs are clearly supplying Mo to the ocean that is isotopically light relative to parent seawater with an end-member isotopic value of $\sim 0.8\%$. As with other components of the Mo budget, the significance of low-temperature or even high-temperature reactions on the Mo budget are, at best, uncertain. For low-temperature systems, input of Mo could be 13% of the riverine source [Wheat et al., 2002], thus making the isotopic composition of ridge-flank derived Mo a potentially important contribution to the Mo isotope balance.

5. Conclusions: Utility of Mo Isotopes in Marine Sedimentary Systems

[16] Marine sedimentary systems demonstrate a systematic fractionation of Mo isotopes with a total dynamic range of $\Delta\delta^{98/95}\text{Mo} = 2.8\%$ for the samples measured here. Data taken from anoxic sediments offer an initial estimate for fractionation during Mo removal with a separation constant of 1.0070. If the fractionation measured here is typical for anoxic systems, then authigenic Mo removal during anoxic diagenesis could fractionate Mo, leaving behind a heavier seawater reservoir (which is observed). We suggest that as a consequence of isotopic fractionation, Mo isotopes may offer a quantitative regional tracer for diagenesis. Such

information could prove valuable on glacial-interglacial timescales where a local change in carbon flux or oxygen minimum zone intensity varies [e.g., Dean et al., 1997]. In addition, the world ocean likely has had large regions of anoxia in the past, yet the chemical records of those events are extremely limited [e.g., Sarmiento et al., 1988; Zhang et al., 2001, and references therein]. Mo isotopes may offer a signature of the magnitude of past oceanic anoxia. Essentially, if diagenesis does fractionate Mo isotopes, then changes in oceanic oxidation state should lead to a Mo isotopic reservoir that is heavier than today, and if records of that reservoir can be established (Mn-crusts? [e.g., Zhang et al., 2001]), they would provide essential paleochemical data.

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